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## VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES

PART XV. THE DISSOCIATION AND POLYMERIZATION ENERGIES OF  
GROUP IV - GROUP VI MOLECULES

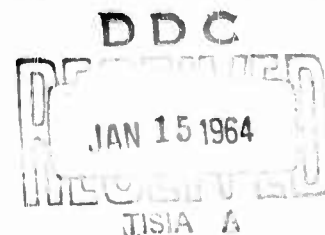
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AF MATERIALS LABORATORY  
RESEARCH AND TECHNOLOGY DIVISION  
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WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Project No. 7350, Task No. 735001

(Prepared under Contract No. AF 61(052)-225 by the  
Universite Libre de Bruxelles, Brussels, Belgium;  
J. Drowart and R. Colin, Authors)



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## FOREWORD

This report was prepared by the University of Brussels, Belgium, under USAF Contract No. AF61(052-225. The contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735001, "Non-Graphitic." The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio. Mr. F. W. Vahldiek was the project engineer.

# ABSTRACT

→ A summary of the mass spectrometric investigation of the vapor phase of group IV-group VI compounds is given. Thermochemically obtained values for the dissociation energies of the MeX molecules are compared to the spectroscopic values. Polymerization energies of MeX and atomization energies of MeX<sub>2</sub><sup>7</sup> molecules are presented. ↗

This technical documentary report has been reviewed and is approved.



W. G. RAMKE

Chief, Ceramics and Graphite Branch  
Metals and Ceramics Division  
Air Force Materials Laboratory

THE DISSOCIATION AND POLYMERIZATION ENERGIES OF  
GROUP IV - GROUP VI MOLECULES<sup>(\*)</sup><sup>(+)</sup>.

J. Drowart and R. Colin

Laboratoire de Chimie Physique Moléculaire  
Université Libre de Bruxelles, Brussels, Belgium.

The diatomic molecules of the Group IV-Group VI elements have been known for a long time from optical spectroscopy, which made it possible to obtain accurate dissociation energies for a number of these molecules<sup>(1,2)</sup>. The condensed compounds of this group, either  $\text{MeX}$  or  $\text{MeX}_2$  are in general also known. Most have been studied thermochemically and total vapor pressures and heats of formation have been measured<sup>(3)</sup>.

Mass spectrometric investigations of the gas phase which concerned  $\text{SiO}_2$ <sup>(4)</sup>,  $\text{PbSe}$ <sup>(5)</sup>,  $\text{PbTe}$ <sup>(5)</sup>,  $\text{SnS}$ <sup>(6)</sup> and  $\text{PbS}$ <sup>(6)</sup> have been extended systematically during the last two years in this laboratory to the remaining compounds<sup>(7)</sup>. These studies made it possible to identify in the gas phase a number of  $(\text{MeX})_n$  polymeric molecules and  $\text{MeX}_2$  molecules and to determine quite accurate values for the dissociation energies of the gaseous  $\text{MeX}$  molecules. A summary of the results is given in the present paper.

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(\*) This work was sponsored in part by the Wright Air Division of the Aeronautical Systems Division A.F.S.C., U.S. Air Force, through its European Office.

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## 1. EXPERIMENTAL.

The mass spectrometer used is a 50°, 20cm radius of curvature, single focussing instrument, adapted<sup>(8)</sup> for the study of high temperature inorganic processes, and equipped<sup>(9)</sup> with a secondary electron multiplier. The samples were placed in Knudsen cells heated by radiation from a tungsten loop and when necessary by electron bombardment. In the studies reported here the latter were mainly quartz cells. Their temperature was measured either with an optical pyrometer or with a Pt-PtRh 10% thermocouple. A molecular beam originating from the cell was collimated and directed into the ion source of the mass spectrometer where the atomic and molecular species were ionized by electron bombardment and then mass analyzed. The identification of the species (Table I) was made in the usual way<sup>(10)</sup> from the mass, appearance potential (Table II) and isotopic distribution of the ions and the intensity distribution in the molecular beam.

## 2. EVALUATION OF THERMODYNAMIC DATA.

The pressures are in general the total pressures given in the literature, corrected, when necessary, for the presence of polymeric species. A number of quantitative vaporization experiments were also carried out to confirm the literature values of the pressure or to complete these. For most of the diatomic molecules the thermodynamic functions are given in the literature<sup>(11,12)</sup>;



whenever not, they were calculated from statistical mechanical formulae using the known molecular parameters<sup>(1)</sup>. Since no information is available for the dimeric species, free energy functions were estimated. Very little is known about the structure of these molecules except that one may think that they are analogous to those of the isoelectronic  $P_4$ ,  $As_4$  and  $Sb_4$  molecules. It was therefore assumed that the free energy functions could be estimated by analogy with those of the  $P_4$ ,  $As_4$  and  $Sb_4$  molecules<sup>(13)</sup>, which implies that a decrease in the symmetry number is compensated by an increase in the vibration frequency. For the higher polymers the free energy functions were estimated by analogy with those of a number of molecules of comparable molecular weight, containing the same total number of atoms<sup>(14)</sup>. For the  $MeX_2$  molecules, which are of the same type as the well known CO, and  $CS_2$  molecules, free energy functions were calculated assuming these molecules to be similar in structure and in nature of the electronic states to the latter molecules. Thermodynamic functions of the condensed phase were taken from the literature whenever available or estimated by methods discussed by Latimer<sup>(16)</sup> and Kubaschewski and Evans<sup>(3)</sup>.

### 3. RESULTS.

#### a) Dissociation Energies.

Table IV gives the dissociation energies derived from thermochemical cycles, based on the heat of sublimation of the

molecule from the condensed phase (Table III), the heat of formation of the latter<sup>(3)</sup> and the heats of sublimation of the elements<sup>(13)</sup>. The thermochemically determined dissociation energies can now be compared to the convergence limits for the electronically excited states observed spectroscopically. Amongst these the best known is that of the E state. It has already been shown previously from rotational analyses that at least for PbO<sup>(16)</sup> and PbS<sup>(17)</sup> this state correlates most probably with the atoms in their  $^3P_1 + ^3P_1$  state. On the basis of the agreement between spectroscopic and thermochemical values for the dissociation energies of SnS and PbS it has also been shown<sup>(6,7)</sup> that the most probable correlation is with the  $^3P_1$  state of the group IV element and the  $^3P_1$  or  $^3P_0$  state of the group VI element. (The small difference between the two mentioned sublevels of the group VI elements makes it difficult to distinguish between them). Table III also gives a comparison between the thermochemically determined dissociation energy and that derived from the electronically excited E state wherever this state is known.

#### b) Polymerization Energies.

The polymerization energies measured to day are summarized in Table V. This table shows that the complexity of the polymers observed is highest for SnO and PbO. It further shows a regular decrease of the dimerization energies from oxides

to tellurides.

The polymerization energies are also compared with the heat of sublimation of monomeric MeX. This heat of sublimation is that of the MeX compound or of the mixture  $\text{MeX}_2 + \text{Me}$ . In those instances where the MeX compound is metastable the heat of the reaction  $1/2 \text{MeX}_2(\text{s}) + \text{Me}(\text{s}) \rightarrow \text{MeX}(\text{s})$  was taken into account. When it is not known it has been assumed equal to zero. From Table II it can be seen that for several molecules the dimerization energy is of the same order of magnitude as the heat of sublimation of the monomer and that the energy required to detach a MeX group from the dimers and more complex polymers is also of the same order of magnitude and tends to show an alternation from even to odd species.

c) MeX<sub>2</sub> molecules.

In addition to the diatomic and polymeric species a number of MeX<sub>2</sub> molecules were observed in these systems. These are analogous to the well known CO<sub>2</sub> and CS<sub>2</sub> molecules to which one analogue was already known, SiO<sub>2</sub><sup>(4)</sup>. Until now the further molecules of this type observed are SiS<sub>2</sub>, SiSe<sub>2</sub>, SiTe<sub>2</sub>, GeTe<sub>2</sub> and SnTe<sub>2</sub>. The atomization energies for these MeX<sub>2</sub> molecules are summarized in Table VI. It is to be noted that for these molecules the ratio of the atomization energy to the dissociation energy of the MeX molecule is quite constant.

TABLE I. Composition of the Vapor of Group IV-Group VI  
compounds

System	Composition of the vapor (in decreasing order of partial pressure).
C + Se <sub>2</sub> (g)	Se <sub>2</sub> , Se, CSe
SiO <sub>2</sub> (4)	SiO, O, SiO <sub>2</sub> , O <sub>2</sub>
SiO <sub>2</sub> + Si (4)	SiO, Si <sub>2</sub> O <sub>2</sub>
SiS + SiS <sub>2</sub>	SiS, S <sub>2</sub> , SiS <sub>2</sub>
SiSe + SiSe <sub>2</sub>	SiSe, Se <sub>2</sub> , SiSe <sub>2</sub>
SiTe + SiTe <sub>2</sub>	Te <sub>2</sub> , SiTe, SiTe <sub>2</sub> , Te
GeO	GeO, Ge <sub>2</sub> O <sub>2</sub> , Ge <sub>3</sub> O <sub>3</sub>
1/2GeO <sub>2</sub> + 1/2Ge	GeO, Ge <sub>2</sub> O <sub>2</sub> , Ge <sub>3</sub> O <sub>3</sub>
GeO <sub>2</sub>	GeO, O <sub>2</sub>
GeS	GeS
GeTe	GeTe, Te <sub>2</sub> , GeTe <sub>2</sub>
1/2SnO <sub>2</sub> + 1/2Sn	SnO, Sn <sub>2</sub> O <sub>2</sub> , Sn <sub>3</sub> O <sub>3</sub> , Sn <sub>4</sub> O <sub>4</sub>
SnS	SnS, Sn <sub>2</sub> S <sub>2</sub>
SnSe	SnSe, Sn <sub>2</sub> Se <sub>2</sub> , Se <sub>2</sub>
SnTe	SnTe, Te <sub>2</sub> , Te, SnTe <sub>2</sub> , Sn <sub>2</sub> Te <sub>2</sub>
PbO	PbO, Pb <sub>2</sub> O <sub>2</sub> , Pb <sub>3</sub> O <sub>3</sub> , Pb <sub>4</sub> O <sub>4</sub>
PbS	PbS, Pb <sub>2</sub> S <sub>2</sub> , Pb, S <sub>2</sub>
PbSe	PbSe, Pb <sub>2</sub> Se <sub>2</sub> , Pb, Se <sub>2</sub>
PbTe (5)	PbTe, Pb, Te, Te <sub>2</sub>

Table II. Appearance potentials of Group IV-Group VI Molecules  
(in eV)

System	MeX	MeX <sub>2</sub>	Me <sub>2</sub> X <sub>2</sub>	Me <sub>3</sub> X <sub>3</sub>	Me <sub>4</sub> X <sub>4</sub>
CO(g) (18)	14.01±0.01				
CO <sub>2</sub> (g) (18)		13.78±0.01			
CS(g) (18)	10.7±0.3				
CS <sub>2</sub> (g) (18)		10.10±0.05			
SiO <sub>2</sub> (4)	(10.8±0.5)	11.7±0.5			
SiO <sub>2</sub> +Si	(10.5±0.5) (19)		10.1±1.0		
SiS+SiS <sub>2</sub>	10.0±0.5	9.5±0.5			
SiSe+SiSe <sub>2</sub>	9.7±0.5				
SiTe+SiTe <sub>2</sub>	9.2±0.5				
GeO	10.1±0.8		8.7±1.0	8.6±1.0	
GeO <sub>2</sub> +Ge					
GeO <sub>2</sub>					
GeS	10.9±0.9				
GeTe	10.1±0.9	10.8±0.5			
SnO <sub>2</sub> +Sn	10.5±0.5		9.8±1.0	9.8±1.0	9.2±1.0
SnO <sub>2</sub>					
SnS	9.7±0.5		9.4±0.5		
SnSe	9.7±0.5				
SnTe	9.1±0.5				
PbO	9.6±0.5		9.3±0.5	11.8±1.0	8.5±0.7
PbS	8.6±0.5		9.2±0.5		
PbSe	8.5±0.5				
PbTe	8.2±0.5				
O <sub>2</sub> (18) : 12.2±0.2 ; S <sub>2</sub> : 9.7±0.5 ; Se <sub>2</sub> : 8.8±0.5 ; Te <sub>2</sub> : 8.4±0.5					

TABLE III. Reaction enthalpies

System	Reaction	$\Delta H_{298}^{\circ}$ kcal/mole
C + Se <sub>2</sub> (g)	C(s) + Se(g) → CSe(g)	- 31.4 ± 2.0
SiO <sub>2</sub> <sup>(4)</sup>	SiO <sub>2</sub> (s) → SiO(g) + 1/2 O <sub>2</sub> (g)	198.3 ± 1.5
SiO <sub>2</sub> + Si <sup>(4)</sup>	1/2 SiO <sub>2</sub> (s) + 1/2 Si(s) → SiO(g)	85.5 ± 0.5
	Si <sub>2</sub> O <sub>2</sub> (g) → 2 SiO(g)	53.5 ± 5.0
SiS + SiS <sub>2</sub>	SiS(s) → SiS(g)	66.3 ± 3.0
	SiS <sub>2</sub> (s) → SiS(g) + 1/2 S <sub>2</sub> (g)	101.5 ± 3.0
	SiS <sub>2</sub> (s) → SiS <sub>2</sub> (g)	70.0 ± 3.0
SiSe + SiSe <sub>2</sub>	SiSe <sub>2</sub> (g) → SiSe(g) + 1/2 Se <sub>2</sub> (g)	25.9 ± 4.0
SiTe + SiTe <sub>2</sub>	SiTe <sub>2</sub> (g) → SiTe(g) + 1/2 Te <sub>2</sub> (g)	21.6 ± 4.0
GeO	GeO(s) → GeO(g)	53.5 ± 2.6
	Ge <sub>2</sub> O <sub>2</sub> (g) → 2 GeO(g)	49.4 ± 4.5
	Ge <sub>3</sub> O <sub>3</sub> (g) → 3 GeO(g)	97.1 ± 7.0
GeO <sub>2</sub> + Ge	1/2 GeO <sub>2</sub> (s) + 1/2 Ge(s) → GeO(g)	58.3 ± 2.2
GeO <sub>2</sub>	GeO <sub>2</sub> (s) → GeO(g) + 1/2 O <sub>2</sub> (g)	121.6 ± 3.0
GeS	GeS(s) → GeS(g)	38.7 ± 0.6
GeTe	GeTe(s) → GeTe(g)	47.2 ± 2.0
	GeTe(s) → Ge(s) + 1/2 Te <sub>2</sub> (g)	24.6 ± 2.0
	2 GeTe(s) → Ge(s) + GeTe <sub>2</sub> (g)	53.3 ± 3.0
	Ge <sub>2</sub> Te <sub>2</sub> (g) → 2 GeTe(g)	< 33

: SnO <sub>2</sub> + Sn :	: 1/2 SnO <sub>2</sub> (s)+1/2Sn(s)->SnO(g):	: 73.6±2.0 :
	: Sn <sub>2</sub> O <sub>2</sub> (g) -> 2SnO(g)	: 69.7±5.0 :
	: Sn <sub>3</sub> O <sub>3</sub> (g) -> 3SnO(g)	: 138.6±7.0 :
	: Sn <sub>4</sub> O <sub>4</sub> (g) -> 4SnO(g)	: 209.2±10.0 :
: SnO <sub>2</sub> :	: SnO <sub>2</sub> (s) -> SnO(g)+1/2O <sub>2</sub> (g) :	: 141.7±2.0 :
: SnS <sup>(6)</sup> :	: SnS(s) -> SnS(g)	: 52.6±1.6 :
	: Sn <sub>2</sub> S <sub>2</sub> (g) -> 2SnS(g)	: 48.7±5.0 :
: SnSe <sup>(22)</sup> :	: SnSe(s) -> SnSe(g)	: 51.0±2.5 :
	: SnSe(s) -> Sn(s)+1/2Se <sub>2</sub> (g)	: 37.0±1.5 :
	: Sn <sub>2</sub> Se <sub>2</sub> (g) -> 2SnSe(g)	: 46.5±5.0 :
: SnTe <sup>(22)</sup> :	: SnTe(s) -> SnTe(g)	: 52.1±2.0 :
	: SnTe(s) -> Sn(s)+1/2Te <sub>2</sub> (g)	: 34.3±2.0 :
	: SnTe(s) -> Sn(s)+Te(g)	: 59.4±4.0 :
	: SnTe <sub>2</sub> (g)-> SnTe(g)+1/2Te <sub>2</sub> (g)	: 17.5±4.0 :
	: Sn <sub>2</sub> Te <sub>2</sub> (g) -> 2SnTe(g)	: 46.8±6.0 :
: PbO :	: PbO(s) -> PbO(g)	: 67.3±2.5 :
	: Pb <sub>2</sub> O <sub>2</sub> (g) -> 2PbO(g)	: 57.3±5.0 :
	: Pb <sub>3</sub> O <sub>3</sub> (g) -> 3PbO(g)	: 114.5±7.0 :
	: Pb <sub>4</sub> O <sub>4</sub> (g) -> 4PbO(g)	: 176.5±10.0 :
: PbS <sup>(6)</sup> :	: PbS(s) -> PbS(g)	: 55.7±1.6 :
	: PbS(s) -> Pb(g)+1/2S <sub>2</sub> (g)	: 84.5±2.6 :
	: Pb <sub>2</sub> S <sub>2</sub> (g) -> 2PbS(g)	: 44.8±5.0 :

PbSe	PbSe(s) -> PbSe(g)	53.9 $\pm$ 2.0
	PbSe(s) -> Pb(s)+1/2Se <sub>2</sub> (g)	41.0 $\pm$ 2.0
	Pb <sub>2</sub> Se <sub>2</sub> (g) -> 2PbSe(g)	44.4 $\pm$ 5.0
PbTe <sup>(5)</sup>	PbTe(s) -> PbTe(g)	55.0 $\pm$ 2.0
	PbTe(g) -> Pb(g)+Te(g)	53.5 $\pm$ 2.0



TABLE IV - Comparison of Spectroscopic ( $D_0^*$ ) and Thermochemical ( $D_0^\circ$ ) Values of the Dissociation Energy of Group IV-Group VI Molecules (in eV).

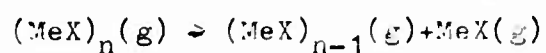
Molecule	Convergence Limit: E State	$D_0^*$ *	$D_0^\circ$
CO		$11.111 \pm 0.06$	
CS			$7.53 \pm 0.15^{(23)}$
CSe			$6.00 \pm 0.15$
(CTe)			$(4.8 \pm 0.4)^{**}$
SiO			$8.32 \pm 0.15$
SiS	$6.44 \pm 0.06^{(24)}$	$6.38 \pm 0.06$	
SiSe	$5.66 \pm 0.15^{(25)}$	$5.40 \pm 0.15$	
SiTe	$(4.70 \pm 0.25)^{(25)}$	$(4.11 \pm 0.25)$	
GeO			$6.82 \pm 0.13$
GeS	$5.79 \pm 0.03^{(26)}$	$5.67 \pm 0.03$	$5.78 \pm 0.15$
GeSe	$5.25 \pm 0.03^{(26)}$	$4.93 \pm 0.03$	
GeTe	$4.49^{+0.30}_{-0.10}^{(26)}$	$^{+0.30}_{-0.10}$	$4.02 \pm 0.15$
SnO	$5.68 \pm 0.05^{(19)}$	$5.45 \pm 0.05$	$5.53 \pm 0.13$
SnS	$5.06 \pm 0.10^{(27)}$	$4.80 \pm 0.10$	$4.78 \pm 0.12^{(6)}$
SnSe	$4.54 \pm 0.05^{(28)}$	$4.08 \pm 0.06$	$4.12 \pm 0.17^{(22)}$
SnTe	$(4.07)^{(28)}$	$(3.28)$	$3.46 \pm 0.17^{(22)}$
PbO	$> 4.86^{(29)}$	$> 3.87$	$4.00 \pm 0.13$
PbS	$4.55 \pm 0.20^{(29)}$	$3.53 \pm 0.20$	$3.42 \pm 0.12^{(6)}$
PbSe	$> 4.32^{(29)}$	$> 3.10$	$3.07 \pm 0.12^{(30)}$
PbTe			$2.30 \pm 0.17$

\* Values based on Birge-Sponer extrapolations have not been included.

\*\* estimated

TABLE V. Enthalpies of Polymerization of Group IV-Group VI

Molecules MeX (in kcal/mole)



Molecule	n=2	n=3	n=4	n=∞ (solid)
SiO	53.5			85.5 *
SiS				66.3
SiSe				
SiTe				
GeO	49.4	47.7		53.1
GeS				38.7
GeSe				
GeTe	≤33			45.3
SnO	59.7	68.9	70.6	73.6
SnS	48.7			52.6
SnSe	46.5			51.0
SnTe	46.8			52.1
PbO	57.3	57.2	62.0	67.3
PbS	44.8			55.7
PbSe	44.4			53.9
PbTe				53.8

\*  $1/2 \text{ MeX}_2(\text{s}) + 1/2 \text{ Me}(\text{s}) \rightarrow \text{MeX}(\text{g})$

TABLE VI. Stability of Group IV-Group VI  $\text{MeX}_2$  Molecules  
(in kcal/mole)

Molecule	$\Delta H^\circ_{\text{at}}(\text{MeX}_2)$	$D^\circ_0(\text{MeX})$	$\Delta H^\circ_{\text{at}}(\text{MeX}_2)/D^\circ_0(\text{MeX})$
$\text{CO}_2/\text{CO}$	381.5	256.2	1.49
$\text{CS}_2/\text{CS}$	272.0	173.6	1.57
$\text{SiO}_2/\text{SiO}$	302.8	191.9	1.58
$\text{SiS}_2/\text{SiS}$	230.4	147.0	1.57
$\text{SiSe}_2/\text{SiSe}$	185.1	124.5	1.49
$\text{SiTe}_2/\text{SiTe}$	140.9	94.7	1.50
$\text{GeTe}_2/\text{GeTe}$	137.1	92.7	1.48
$\text{SnTe}_2/\text{SnTe}$	123.2	79.8	1.55

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